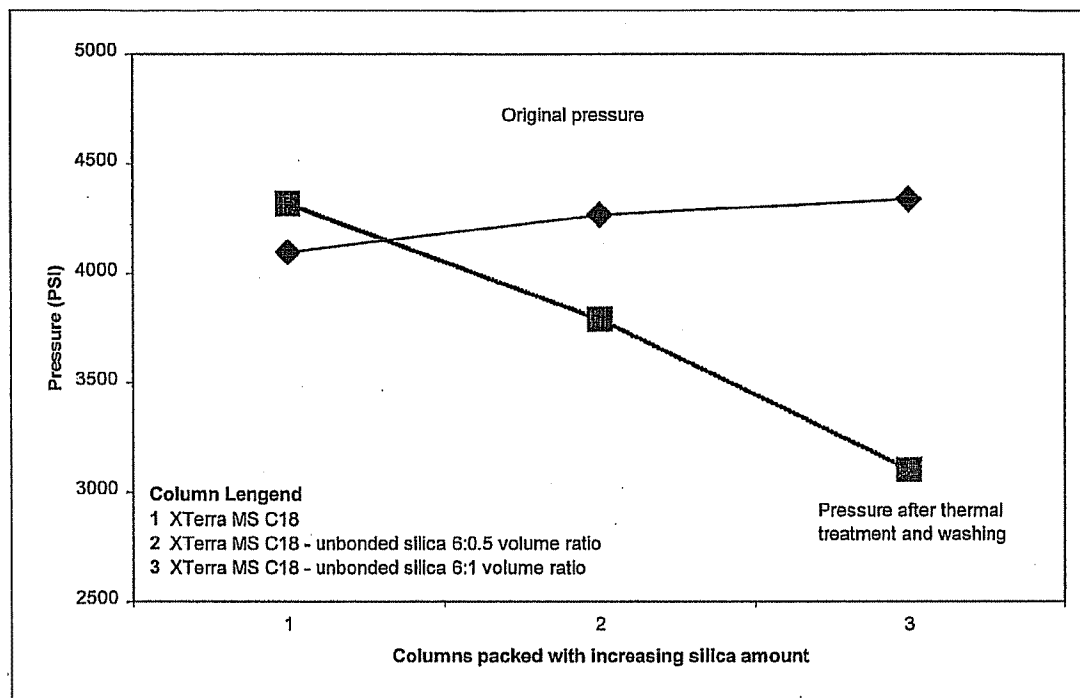


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FIGURE 1



5

EXAMPLE 29

Pluronic P-105, 0.7 g, (from BASF Corp., Mount Olive, NJ) was dissolved in 5mL of an acetic acid solution selected from the following concentrations, respectively: 30mM, 50mM, 70mM, and 110mM. The resulting solution was agitated at room temperature until all of the Pluronic P-105 was dissolved and was then chilled in an ice-water bath.

Meanwhile, methyltrimethoxysilane, 5mL, and tetramethoxysilane, 10mL, (both from Gelest Inc., Tullytown, PA) were mixed at room temperature in a separate, sealed flask. An aliquot of 2mL of the mixed silane solution was slowly added into the chilled acetic acid mixture, whereupon the silanes dissolved into the acetic acid solution after a few minutes. The resulting transparent solution was transferred into a sealed polypropylene container (9.6mm x 10cm) and kept at 45 °C undisturbed for 2 days. The solid white rod produced was subsequently immersed into 100 mL 0.1 N aqueous ammonium hydroxide solution for 3 days at 60 °C. The monolith material was then washed with water for 2 days, solvent-exchanged to methanol for 1 day, and then dried

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in air for 5 hours. The monolith material was then dried under vacuum at 135 °C for 3 days, resulting in a white rod without any cracks.

The morphologies of the formed rods were observed by a scanning electron microscope. It was observed that a three-dimensional interconnected network was formed within the rods and that the skeleton thickness increased as the acetic acid concentration increased. As listed in Table 11, the monolith material obtained from 30mM acetic acid solution had a skeleton thickness less than 0.5 μm , while the monolith material obtained from 110mM acetic acid solution had a skeleton thickness around 5 μm .

Median pore diameter (MPD) and pore volume (PV) of thus formed rods were measured by Mercury Porosimetry. The specific surface areas (SSA), specific pore volumes (SPV) and the average pore size diameters (APD) of the mesopores were measured using the multi-point N_2 sorption method. Results are compiled in Table 11. The specific surface area was calculated using the BET method, the specific pore volume was the single point value determined for $P/P_0 > 0.98$, and the average pore diameter was calculated from the desorption leg of the isotherm using the BJH method.

TABLE 11

Product	Acetic Acid Concentration (mM)	Skeleton Thickness (μm)	MPD (μm)	PV(1) (cc/g)	MPD (\AA)	PV(2) (cc/g)	SSA (m^2/g)	SPV (cc/g)	APD (\AA)
29a	30	<0.5	0.3	4.5	-	-	850	1.98	92
29b	50	0.7	0.35	4.0	-	-	841	1.96	92
29c	70	2	2.2	3.12	265	1.62	682	1.81	102
29d	110	5	16.3	2.61	139	0.96	939	1.33	57

EXAMPLE 30

Triton X-100, 0.7 g, (Aldrich Chemical, Milwaukee, WI) was dissolved in 5mL of an acetic acid solution selected from the following concentrations, respectively: 40mM and 80mM. The resulting solution was agitated at room temperature until all of the Triton X-100 was dissolved and was then chilled in an ice-water bath.

Meanwhile, methyltrimethoxysilane, 5mL, and tetramethoxysilane, 10mL, (both from Gelest Inc., Tullytown, PA) were mixed at room temperature in a separate, sealed flask. An aliquot of 2mL of the mixed silane solution was slowly added into the chilled acetic acid mixture, whereupon the silanes dissolved into the acetic acid solution after a

few minutes. The resulting transparent solution was transferred into a sealed polypropylene container (9.6mm x 10cm) and kept at 45 °C undisturbed for 2 days. The solid white rod produced was subsequently immersed into 100 mL 0.1 N aqueous ammonium hydroxide solution for 3 days at 60 °C. The monolith material was then
5 washed with water for 2 days, solvent-exchanged to methanol for 1 day, and then dried in air for 5 hours. The monolith material was then dried under vacuum at 135 °C for 3 days, resulting in a white monolith material without any cracks.

The morphologies of the formed rods were observed by a scanning electron microscope. It was observed that a three-dimensional interconnected network was
10 formed within the rods and that the skeleton thickness increased as the acetic acid concentration increased. For example, the monolith material obtained from 40mM acetic acid solution had a skeleton thickness less than 0.5 μm , while the monolith material obtained from 80mM acetic acid solution had a skeleton thickness around 4 μm .

Pore size characterization of the monolith material prepared from 80mM acetic
15 acid is listed in Table 12.

TABLE 12

Product	Acetic Acid Concentration (mM)	Skeleton Thickness (μm)	MPD (μm)	PV(1) (cc/g)	MPD (\AA)	PV(2) (cc/g)	SSA (m^2/g)	SPV (cc/g)	APD (\AA)
30	80	4	4.5	2.8	161	1.23	673	1.3	79

20

EXAMPLE 31

The following experiment was carried out in order to demonstrate the relationship between skeleton thickness and incubation time. Rods were prepared from the same sol composition and processed under similar conditions except with different
25 incubation times.

Pluronic P-105, 0.7g, was dissolved in a 90mM acetic acid solution. The resulting solution was agitated at room temperature until the Pluronic P-105 was completely dissolved and then chilled in an ice-water bath.

Meanwhile, methyltrimethoxysilane, 5mL, and tetramethoxysilane, 10mL, (both
30 from Gelest Inc., Tullytown, PA) were mixed at room temperature in a separate, sealed flask. An aliquot of 2mL of the mixed silane solution was slowly added into the chilled acetic acid mixture, whereupon the silanes dissolved into the acetic acid solution after a few minutes. The resulting transparent solution was transferred into a sealed polypropylene container (9.6mm x 10cm) and kept at 45 °C undisturbed for 45 hours.

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The process was repeated in the same manner except the resulting transparent solution was kept undisturbed for 112 hours.

The solid white rods produced were subsequently immersed into 100 mL 0.1 N aqueous ammonium hydroxide solution for 3 days at 60 °C. The monolith materials
5 were then washed with water for 2 days, solvent-exchanged to methanol for 1 day, and then dried in air for 5 hours. The monolith materials were then dried under vacuum at 135 °C for 3 days, resulting in a white monolith material without any cracks.

The morphologies of the formed rods were observed by a scanning electron
10 microscope. Both rods were determined to have a three dimensional interconnected skeleton network, and a skeleton thickness that increased as the incubation time increased. The material with a 112 h incubating time had a skeleton thickness around 5 μm , while the one with a 45 h incubating time had a skeleton thickness of 3.5 μm .

15

EXAMPLE 32

The hybrid inorganic/organic monolith material rods prepared in Example 29 and
30 were immersed in 100mL of 0.1 N tris(hydroxymethyl)aminomethane (TRIS, Aldrich
Chemical, Milwaukee, WI) in water. The pH of the solution was adjusted to 8.0 by
adding concentrated acetic acid. The resulting solution was then enclosed in a stainless
20 steel autoclave and heated to 155 °C for 24 hours. After the autoclave cooled to room
temperature, the monolith material was rinsed with water for 2 days, with methanol for 1
day, and then dried in air for 4 hours. The monolith material was then dried under
vacuum at 100 °C for 1 day.

Pore size characteristics of the resulting rods were determined using mercury
25 porosimetry and multi-point N_2 sorption BET method, and the results are compiled in
Table 13. An example of the pore size over pore volume relationship, or the mesopore
size distribution, before and after subjection to the hydrothermal autoclave process is
graphed in Figure 2, which demonstrate that the hydrothermal process narrowed the
mesopore size distribution.

30

35

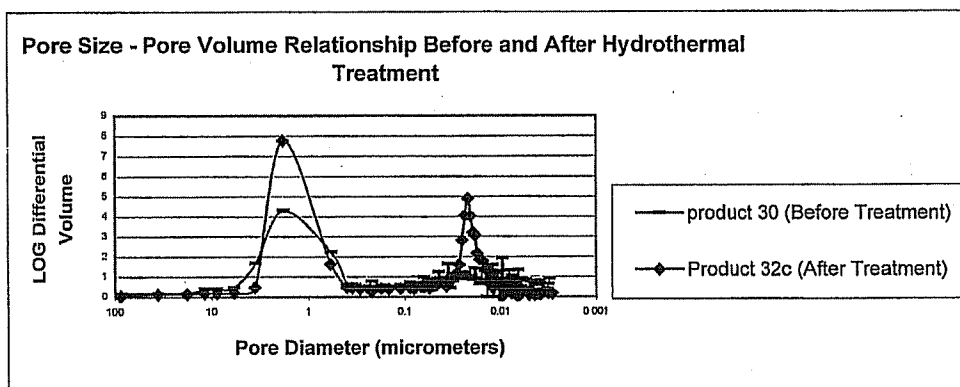
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TABLE 13

Product #	Product # Before Hydrothermal Treatment	Acetic Acid Concentration (mM)	Template	SSA (m ² /g)	SPV (cc/g)	APD (Å)
32a	29c	70	Pluronic P-105	284	1.51	256
32b	29d	110		176	1.19	264
32c	30	80	Triton X-100	173	1.46	322

5

FIGURE 2



EXAMPLE 33

10 Three rods were prepared in a similar fashion to product 29c and were separately immersed in 100mL 0.1 N tris(hydroxymethyl)aminomethane (TRIS, Aldrich Chemical, Milwaukee, WI) water solutions. The hydrothermal process conditions, such as pH and temperature, of the three reactions are listed in Table 14.

15 Pore size characteristics of the final materials using the BET method are compiled in Table 14. As depicted, average pore size decreases both as the pH decreases and as the temperature decreases for the hydrothermal process.

20

TABLE 14

Product #	pH of 0.1N TRIS Solution	Temperature of Hydrothermal Process	SSA (m ² /g)	SPV (cc/g)	APD (Å)
33a	8.0	155 °C	284	1.51	256
33b	8.0	130 °C	324	1.58	238
33c	7.5	130 °C	379	1.72	209

5

EXAMPLE 34

A 1.03 g amount of the dried monolith material (product 33a of Example 33) was soaked in 20 mL of toluene (J.T. Baker) and refluxed for 3.5 h under an argon atmosphere to deoxygenate and removed adsorbed water *via* azeotropic distillation. After cooling to room temperature under dry argon, 0.42 g of imidazole (Aldrich Chemical) and 0.784 g of n-octadecyltriethoxysilane (Gelest Inc., Tullytown, PA) were added. The solution was stirred and heated to 105 °C for 20h. The monolith material, after cooling, was exhaustively washed with toluene and acetone (J.T. Baker). The washed monolith material was dried at 80 °C under vacuum for 24 h. The surface concentration ($\mu\text{mol}/\text{m}^2$) of n-octadecylsilane was determined by the difference in the monolith material carbon content before and after the surface modification as measured by elemental analysis. The resulting monolith material had a 4 % increase in carbon content that is analogous to a surface coverage of 0.7 ($\mu\text{mol}/\text{m}^2$) of n-octadecylsilane group.

20

EXAMPLE 35

A solution was prepared consisting of 5 mL of Sylgard 184® Part A and 0.5 mL Sylgard 184® Part B (both from Dow Corning Corp., Midland, MI) in 100 mL ethyl acetate (HPLC grade, J.T. Baker). Octadecyl (C_{18}) functionalized and end capped hybrid particles of product type 25u in Example 25 were then suspended in the Sylgard®/ethyl acetate solution in a ratio of 100 mg particles per 1 milliliter of solution. The mixture was agitated manually to wet the particles, and the suspension was sonicated for 2 minutes (Branson 5510 ultrasonic bath or equivalent, Branson Ultrasonic Corp., Danbury, CT). The particles were then isolated by vacuum filtration (0.5 μm Tyvek® filter paper or equivalent, DuPont, Wilmington, DE), which was monitored and stopped when the gross liquid was removed from the filter cake. The filter cakes were allowed to

"air dry" at room temperature for 2 days and were then vacuum dried at 70°C and < 15mm Hg.

- 5 The Sylgard 184® pre-coated particles, 4.80 g, were combined with 1.20 g of 5µm spherical Symmetry silica particles (Waters Corporation) in a 50 mL polypropylene bottle. The mixture was blended manually for 5 minutes, and the mixed particles were then slurry packed into 2.1 x 50 mm HPLC columns using a downward slurry technique. The column packing apparatus comprised a high-pressure liquid packing pump (Model No: 10-500FS100 or equivalent, SC Hydraulic Engineering Corp., Los Angeles, CA) and a slurry packing reservoir (15 mL), which was connected to the assembled column.
- 10 A slurry of the mixed stationary phase was prepared in tetrahydrofuran - isopropanol 70:30 (v/v) mixture, sonicated for 5 min and poured into the packing reservoir. The reservoir was then closed and methanol was pumped through the column to a pressure of 9000-9500 PSI. After sufficient time for bed consolidation the pump was turned off, and the pressure was released.
- 15 The packed columns were purged with methanol and then ethyl acetate at 0.4 mL/min flow rate using a high pressure chromatography pump (Waters 590 HPLC pump or equivalent), whereupon greater than 10 mL of each purge solvent was collected. A Sylgard 184® solution was prepared by dissolving 15 mL Sylgard 184® Part A and 1.5 mL Sylgard 184® Part B in 100 mL ethyl acetate. The solutions were used either within
- 20 2 hours of preparation or after allowing pre-polymerization (aging) for 3, 25 and 72 hours, respectively. The Sylgard 184® solutions were pumped through packed columns (see above) separately at 0.2mL/min flow rate using a Waters 590 HPLC pump until 3 mL of effluent was collected. The column pressure was allowed to drop for 30 minutes prior to disconnection. The columns were left uncapped in a chemical fume hood's air
- 25 stream for 18 h, transferred to a 65°C convection oven for 28 h, and then cooled to room temperature. The coalesced particle hybrid monoliths were then extruded from the columns and vacuum dried for 7.5 h at room temperature.

- 30 The specific surface area (SSA), specific pore volumes (SPV) and the average pore diameters (APD) of the resultant materials are listed in Table 15 and were measured using the multi-point N₂ sorption method (Micromeritics ASAP 2400 instrument or equivalent, Micromeritics, Norcross, GA). The specific surface area was calculated using the BET method, the specific pore volume was the single point value determined at $P/P_0 > 0.98$, and the average pore diameter was calculated from the desorption leg of the isotherm using the BJH method.

5

Table 15

Product	Sylgard® treatment	Pre-polymerization time of Sylgard 184® solution	Coalesced particles observed by SEM?	SSA (m ² /g)	SPV (cm ³ /g)	APD (Å)
35a	Yes	< 2 hours	No	113	0.42	114
35b	Yes	3 hours	Yes	119	0.45	115
35c	Yes	25 hours	Yes	120	0.45	114
35d	Yes	72 hours	Partial	118	0.44	116
Control	None	NA	NA	129	0.48	117

EXAMPLE 36

- 10 A non-ionic surfactant, Pluronic P-105 (P-105; BASF, Mount Olive, NJ) or Triton X-100 (X-100; Aldrich Chemical) was dissolved in a glacial acetic acid (J.T. Baker) and water solution. To this solution, a mixture of methyltrimethoxysilane and tetramethoxysilane (both from Gelest Inc.) was added at 0°C with stirring for 30 min. The resulting solution was sealed in a glass vial and kept at 45°C for 3 days. The
- 15 solution solidified, and a white solid rod was produced. Thus rod was then immersed into an 1 M ammonium hydroxide (J.T. Baker) water solution at 60 °C for 3 days. After washing out the ammonium hydroxide using water, the rod was immersed in a tris(hydroxymethyl) aminomethane (TRIS; Aldrich Chemical) and water solution. The pH of the solution was then adjusted as desired by adding glacial acetic acid (J.T.
- 20 Baker). The resulting solution and immersed rod was then enclosed in a stainless steel autoclave and heated to 155 °C for 24 h.

After the autoclave cooled down to room temperature, the rod was washed repeatedly with water and methanol, dried in the air for 4 h, and then vacuum dried at 80 °C for 1 day. Detailed reagent amounts and reaction conditions used to prepare these

25 hybrid monolith materials are listed in Table 16. The post hydrothermal compositions were confirmed using combustion analysis or %CHN (CE-440 Elemental Analyzer or equivalent; Exeter Analytical Inc., North Chelmsford, MA), ¹³C and ²⁹Si CPMAS NMR

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spectroscopy (Bruker MSL-300 NMR spectrometer or equivalent, Bruker, Billerica, MA).

The median macropore diameter (MPD) and macropore pore volume (MPV) of the resultant materials was measured by Mercury Porosimetry (Micromeritics AutoPore II 9220 or AutoPore IV or equivalent, Micromeritics, Norcross, GA) and are listed in Table 17. The specific surface area (SSA), specific pore volumes (SPV), and average pore diameters (APD) of the resultant materials are listed in Table 17 and were measured and calculated as described in Example 35. The micropore surface area (MPA), which is defined as the surface area in pores with diameters less than or equal to 34 Å, was also determined from the adsorption leg of the isotherm using the BJH method.

EXAMPLE 37

A non-ionic surfactant, Pluronic P-105 (P-105; BASF) or Pluronic P-123 (P-123; BASF) was dissolved in a glacial acetic acid (J.T. Baker) water solution. To this solution, a mixture of 1,2-bis-(trimethoxysilyl)ethane (Aldrich Chemical) and tetramethoxysilane (Gelest Inc.) was added at 0°C with stirring for 30 min. The resulting solution was sealed in a glass vial and kept at 45°C for 2 days. The solution solidified, and a white solid rod was produced, which was then immersed into an 1 M ammonium hydroxide (J.T. Baker) water solution at 60 °C for 2 days. After washing out the ammonium hydroxide using water, the rod was immersed in a tris(hydroxymethyl)aminomethane (TRIS, Aldrich Chemical) and water solution. The pH of the solution was then adjusted as desired by adding glacial acetic acid (J.T. Baker). The resulting solution and immersed rod was then enclosed in a stainless steel autoclave and heated to 155 °C for 24 h.

After the autoclave cooled down to room temperature, the rod was washed repeatedly with water and methanol, dried in the air for 4 h, and then vacuum dried at 80 °C for 1 day. Detailed reagent amounts and reaction conditions to prepare these hybrid monolith materials are listed in Table 16. The post hydrothermal compositions were confirmed using %CHN, ¹³C and ²⁹Si CPMAS NMR spectroscopy as described in Example 36.

The median macropore diameter (MPD) and macropore pore volume (MPV) of these resultant materials are listed in Table 17 and were measured as described in Example 36. The specific surface area (SSA), specific pore volume (SPV), average pore diameter (APD), and micropore surface area (MPA) of these resultant materials are listed in Table 13 were measured and calculated as described in Examples 35 and 36.

EXAMPLE 38

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- A non-ionic surfactant, Triton 405 (405; Aldrich Chemical) or Triton X-100 (X-100; Aldrich Chemical) was dissolved in a glacial acetic acid (J.T. Baker) water solution. To this solution, a mixture of methacryloxypropyltrimethoxysilane and tetramethoxysilane (both from Gelest Inc.) was added at 0°C with stirring for 30 min.
- 5 The resulting solution was sealed in a glass vial and kept at 45°C for 3 days. The solution solidified, and white solid rod was produced, which was then immersed into an 1 M ammonium hydroxide (J.T. Baker) water solution at 60 °C for 3 days. After washing out the ammonium hydroxide using water, the rod was immersed in a tris(hydroxymethyl)aminomethane (TRIS, Aldrich Chemical) and water solution. The
- 10 pH of the solution was then adjusted as desired by adding glacial acetic acid (J.T. Baker). The resulting solution and immersed rod was then enclosed in a stainless steel autoclave and heated to 155 °C for 24 h.

- After the autoclave cooled down to room temperature, the rod was washed repeatedly with water and methanol, dried in the air for 4 h, and then vacuum dried at 80
- 15 °C for 1 day. Detailed reagent amounts and reaction conditions to prepare these hybrid monolith materials are listed in Table 16.

- The methacryloxypropyl group of the hybrid materials were converted into a 3-hydroxypropyl group *via* hydrolysis of the ester bond during hydrothermal treatment in the autoclave. The post hydrothermal treatment composition of the hybrid material's
- 20 organic substituent is thus described as a 3-hydroxypropyl or propanol [$\text{HO}(\text{CH}_2)_3\text{SiO}_{1.5}$] group. Conversion of the ester into the alcohol group was observed by a decrease in the %C of the rods before vs. after treatment. The post hydrothermal compositions were confirmed using %C, ^{13}C and ^{29}Si CPMAS NMR spectroscopy as described in Example 36.

- 25 The median macropore diameter (MPD) and macropore pore volume (MPV) of these resultant materials are listed in Table 13 and were measured as described in Example 36. The specific surface area (SSA), specific pore volume (SPV), average pore diameter (APD), and micropore surface area (MPA) of these resultant materials are listed in Table 17 and were measured as described in Examples 35 and 36.

Table 16

Product	Post-Hydrothermal Composition of Hybrid Material	Hydrothermal TRIS Conditions									
		Surfactant Type	Surfactant (g)	Acetic Acid (mg)	Water (mL)	TMOS (mL)	RTMOS (mL)	Amount (mL/g)	Conc. (Molarity)	pH	Temp. (°C)
36a	$\text{SiO}_2/(\text{CH}_3\text{SiO}_{1.5})_{0.5}$	P-105	2.8	84	20	5.33	2.67	210	0.1	8.0	155
36b	$\text{SiO}_2/(\text{CH}_3\text{SiO}_{1.5})_{0.5}$	P-105	0.7	27	5	1.33	0.67	160	0.1	8.9	155
36c	$\text{SiO}_2/(\text{CH}_3\text{SiO}_{1.5})_{0.5}$	P-105	0.7	33	5	1.33	0.67	500	0.1	8.0	155
36d	$\text{SiO}_2/(\text{CH}_3\text{SiO}_{1.5})_{0.5}$	X-100	0.7	24	5	1.33	0.67	350	0.1	8.0	155
37a	$\text{SiO}_2/(\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_{0.15}$	P-105	0.8	27	5	1.6	0.4	70	0.1	8.0	155
37b	$\text{SiO}_2/(\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_{0.15}$	P-105	0.9	27	5	1.6	0.4	70	0.1	8.0	155
37c	$\text{SiO}_2/(\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_{0.15}$	P-105	0.7	27	5	1.6	0.4	200	0.3	9.0	155
37d	$\text{SiO}_2/(\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_{0.25}$	P-123	0.7	30	5	1.43	0.57	100	0.3	10.6	155
37e	$\text{SiO}_2/(\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_{0.25}$	P-123	0.6	30	5	1.43	0.57	200	0.1	10.6	155
37f	$\text{SiO}_2/(\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_{0.25}$	P-123	0.65	30	5	1.43	0.57	200	0.1	10.6	155
37g	$\text{SiO}_2/(\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_{0.25}$	P-123	14.1	600	100	28.6	11.4	20	0.1	10.5	155
38a	$\text{SiO}_2/[\text{HO}(\text{CH}_2)_3\text{SiO}_{1.5}]_{0.15}$	X-100	0.7	4.2	5	1.6	0.4	670	1.2	10.6	155
38b	$\text{SiO}_2/[\text{HO}(\text{CH}_2)_3\text{SiO}_{1.5}]_{0.15}$	405	0.7	4.2	5	1.6	0.4	670	1.2	10.6	155
38c	$\text{SiO}_2/[\text{HO}(\text{CH}_2)_3\text{SiO}_{1.5}]_{0.15}$	X-100	1.31	4.2	5	1.6	0.4	80	0.1	8.0	155

Table 17

Product	MPD (μm)	MPV (cc/g)	SSA (m^2/g)	SPV (cc/g)	APD (\AA)	MPA (m^2/g)
36a	2.4	3.56	284	1.51	256	126
36b	6.2	2.75	171	1.22	179	42
36c	17.6	0.85	177	1.19	264	50
36d	5.4	2.8	173	1.46	322	47
37a	2.98	3.11	186	1.47	203	7
37b	0.76	2.91	220	1.89	237	21
37c	4.7	1.38	214	1.91	290	59
37d	4.4	2.42	171	1.29	219	9
37e	1.34	2.1	130	1.04	240	14
37f	1.21	2.11	141	1.12	246	14
37g	2.14	3.7	208	1.4	197	7
38a	5.1	3.15	162	0.96	234	37
38b	28.2	3.15	151	0.81	214	39
38c	1.5	2.77	260	0.71	77	20

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EXAMPLE 39

Hybrid monoliths prepared according to Examples 36, 37, and 38 were immersed in a 1 M hydrochloric acid solution (Aldrich Chemical) for 24 h at 98 °C. After acid treatment was complete, the monoliths were washed with water to a pH above 5 followed by acetone washing (J.T. Baker). The monoliths were then dried at 80 °C under vacuum for 24 h.

EXAMPLE 40

Hybrid monoliths prepared according to example 36a and 37a were acid washed according to Example 39. The hybrid monoliths were then immersed into 2100 mL toluene and heated to reflux for 2h to remove residual water by azeotropic distillation. Under a blanket of argon protection, the reaction was cooled to room temperature, and 16.3 g of octadecyltrichlorosilane (Aldrich Chemical) and 3.43 g of imidazole (from ACROS, Pittsburgh, PA) were slowly added to the reaction mixture. The reaction was then heated to 110 °C for 24h.

The monoliths were subsequently washed twice with fresh toluene at 110 °C for 30 min, and washed twice with acetone at room temperature, for 30 min. Without drying, the monoliths were immersed into 2100 mL of 0.12 M ammonium acetate solution and heated to 60 °C for 2h. The monoliths were then washed by water and acetone and dried under vacuum at 80 °C for 24h. The surface concentration ($\mu\text{mol}/\text{m}^2$) of n-octadecylsilane was determined by the difference in the monolith material %C content before and after the surface modification as measured by %C (CE-440 Elemental Analyzer or equivalent; Exeter Analytical Inc., North Chelmsford, MA)

A second step surface modification (or end capping) of the previously modified monoliths was performed with chlorotrimethylsilane (Aldrich Chemical). Accordingly, ODS modified monoliths were immersed into 2L toluene and heated to reflux for 2h to remove any residue water by azeotropic distillation. Under a blanket of argon protection, the reaction was cooled down to room temperature, and 4.56 g of chlorotrimethylsilane and 3.43 g of imidazole (from ACROS) were slowly added to the reaction mixture. The reaction was then heated to 110 °C for 4h.

The monoliths were subsequently washed twice with fresh toluene at 110 °C for 30 min, washed twice with acetone at room temperature, for 30 min, and dried under vacuum at 80 °C for 24h. The carbon content was measured by combustion analysis as described in Example 36. Table 18 lists the monolith materials used in the reaction, the surface concentration of the resultant bonded octadecylsilane (ODS) group, and the total %C of the final monolith after end capping.

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Table 18

Product	Hybrid Material Prior to ODS Modification	Hybrid Material (g)	ODS Surface Concentration ($\mu\text{mol}/\text{m}^2$)	%C Final Modified Monolith
40a	36a	12.5	2.84	21.97
40b	37a	16.0	1.92	18.16

EXAMPLE 41

5 Hybrid monoliths prepared according to example 38a were acid washed according to Example 39. The hybrid monoliths (1 g) were then immersed into 30 mL toluene and heated to reflux for 2h to remove any residual water by azeotropic distillation. Under a blanket of argon protection, the reaction was cooled down to room temperature, and 0.61g of dodecylisocyanate (Aldrich Chemical) was slowly added. The
10 reaction was then heated to 110 °C for 24h.

The monoliths were subsequently washed with fresh toluene and acetone twice each at room temperature, for 30 min. Without drying, the monoliths were immersed into 100 mL 1% trifluoroacetic acid acetone/water solution (v/v 1/1) and heated to 60 °C for 30 min. The monoliths were then washed by water and acetone, and dried under
15 vacuum at 80 °C for 24h. The reaction of the dodecyl isocyanate molecule with the hybrid monolith's hydroxyl group to form a carbamate group and thereby connect the dodecyl chain to the monolith's skeletal structure through a covalent organic bond was established by a 10.84 %C difference in the monolith material carbon content before and after the surface modification. The %C was measured by combustion analysis as
20 described in Example 36. That increase in %C is analogous to a surface concentration of 2.76 $\mu\text{mol}/\text{m}^2$ of O-propylsilyl N-dodecyl carbamate groups. Furthermore, ^{13}C CPMAS NMR spectroscopy of the particles showed resonances consistent with addition product, where 40% of the propanol groups were converted to carbamate groups, and the remaining propanol groups remained unreacted.

25

EXAMPLE 42

Hybrid monoliths prepared according to example 38a were acid washed
30 according to Example 39. In a three-neck flask, 1g of the hybrid monoliths were immersed into a mixture of 50 mL tetrahydrofuran, 0.72g 1,2-epoxydodecane, and 0.06g iron(III) chloride (all from Aldrich Chemical) at room temperature. The mixture was kept at room temperature with stirring for 4 h. The hybrid monolith was then removed

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from the reaction mixture and extensively washed with 1% (by w%) hydrochloric acid water solution, acetone/water, and acetone. The monoliths were then dried under vacuum at 80 °C for 24h.

Reaction of the 1,2-epoxydodecane molecule with the hybrid monolith's hydroxyl group to form a hydroxyl substituted ether group and thereby connect the decyl chain to the monolith's skeletal structure through a covalent organic bond was established by a 6.55 %C difference in the monolith material carbon content before and after the surface modification. The %C was measured by combustion analysis as described in Example 30. That increase in %C is analogous to a surface concentration of 1.80 $\mu\text{mol}/\text{m}^2$ of decyl ether groups. Furthermore, ^{13}C CPMAS NMR spectroscopy of the particles showed resonances consistent with addition product, where 30% of the propanol groups were converted to ether groups, and the remaining propanol groups remained unreacted.

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EXAMPLE 43

Hybrid monoliths prepared according to example 38a were acid washed according to Example 39. A 1g quantity of the hybrid monoliths was then immersed into 1000 mL toluene with 0.37g p-toluenesulfonic acid monohydrate (Aldrich Chemical) and heated to reflux for 2h to remove any residual water by azeotropic distillation. Under a blanket of argon protection, an additional funnel filled with a mixture of 15 mL toluene and 3.07 g of n-decylalcohol (Aldrich Chemical) was attached directly onto the top of the flask, and the solution was slowly added to the reaction mixture over a period of 2 h. The reaction was then heated to reflux for 24h, whereupon the water generated as one of the reaction products was continually removed by azeotropic distillation. After the reaction was cooled down, the monoliths were then washed by water and acetone, and dried under vacuum at 80 °C for 24h.

The reaction of the n-decylalcohol molecule with the hybrid monolith's hydroxyl group to form an ether group and thereby connect the decyl chain to the monolith's skeletal structure through a covalent organic bond was established by a 6.04 %C difference in the monolith material carbon content before and after the surface modification. The %C was measured by combustion analysis as described in Example 36. That increase in %C is analogous to a surface concentration of 1.66 $\mu\text{mol}/\text{m}^2$ of decyl ether groups. Furthermore, ^{13}C CPMAS NMR spectroscopy of the particles showed resonances consistent with addition product, where 30% of the propanol groups were converted to ether groups, and the remaining propanol groups remained unreacted.

Incorporation By Reference

5 The entire contents of all patents, published patent applications and other references cited herein are hereby expressly incorporated herein in their entireties by reference.

Equivalents

10 Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents were considered to be within the scope of this invention and are covered by the following claims. The contents of all references, issued patents, and published patent applications cited throughout this application are hereby incorporated by reference.

What is claimed is:

1. A porous inorganic/organic hybrid monolith material, comprising a chromatographically-enhancing pore geometry.
- 5 2. A porous inorganic/organic hybrid monolith material, wherein pores of a diameter of less than about 34Å contribute less than about 110 m²/g to less than about 50 m²/g to the specific surface area of the material.
3. A porous inorganic/organic hybrid monolith material, comprising coalesced porous inorganic/organic hybrid particles having a chromatographically-enhancing pore
10 geometry.
4. A porous inorganic/organic hybrid monolith material, comprising coalesced porous inorganic/organic hybrid particles that have a chromatographically-enhancing pore geometry, wherein said particles have been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group
15 surface modifier, a polymeric coating surface modifier, and combinations thereof,
5. The hybrid monolith material of claim 3, wherein said hybrid particles have been surface modified with a surface modifier having the formula $Z_a(R')_bSi-R$, where $Z = Cl, Br, I, C_1 - C_5$ alkoxy, dialkylamino or trifluoromethanesulfonate; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $C_1 - C_6$ straight, cyclic or branched
20 alkyl group, and R is a functionalizing group.
6. The hybrid monolith material of claim 3, wherein said hybrid particles have a specific surface area of about 50 to 800m²/g.
7. The hybrid monolith material of claim 3, wherein said hybrid particles have a specific surface area of about 75 to 600m²/g.
- 25 8. The hybrid monolith material of claim 3, wherein said hybrid particles have a specific surface area of about 100 to 350m²/g.
9. The hybrid monolith material of claim 3, wherein said hybrid particles have specific pore volumes of about 0.25 to 1.5 cm³/g.
10. The hybrid monolith material of claim 3, wherein said hybrid particles have
30 specific pore volumes of about 0.4 to 1.2 cm³/g.
11. The hybrid monolith material of claim 3, wherein said hybrid particles have a micropore surface area of less than about 110 m²/g.
12. The hybrid monolith material of claim 11, wherein said hybrid particles have a micropore surface area of less than about 105 m²/g.

13. The hybrid monolith material of claim 11, wherein said hybrid particles have a micropore surface area of less than about 80 m²/g.
14. The hybrid monolith material of claim 11, wherein said hybrid particles have a micropore surface area of less than about 50 m²/g.
- 5 15. The hybrid monolith material of claim 3, wherein said hybrid particles have an average pore diameter of about 50 to 500 Å.
16. The hybrid monolith material of claim 3, wherein said hybrid particles have an average pore diameter of about 100 to 300 Å.
17. The hybrid monolith material of claim 3, wherein said hybrid particles have a
10 specific surface area of about 50 to 800 m²/g, said hybrid particles have specific pore volumes of about 0.25 to 1.5 cm³/g, and said hybrid particles have an average pore diameter of about 50 to 500 Å.
18. The hybrid monolith material of claim 3 or 4, wherein said hybrid particles have been surface modified by coating with a polymer.
- 15 19. The hybrid monolith material of claim 18, wherein said polymer is Sylgard®.
20. The hybrid monolith material of claim 5, wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl, hexyl and cyclohexyl.
21. The hybrid monolith material of claim 5, wherein the functionalizing group R is
20 selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, or an alkyl or aryl group containing an embedded polar functionality.
22. The hybrid monolith material of claim 21, wherein said functionalizing group R is a C₁ – C₃₀ alkyl group.
- 25 23. The hybrid monolith material of claim 21, wherein said functionalizing group R is a C₁ – C₂₀ alkyl group.
24. The hybrid monolith material of claim 4, wherein said surface modifier is selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octyldimethylchlorosilane, and octadecyldimethylchlorosilane.
- 30 25. The hybrid monolith material of claim 24, wherein said surface modifier is selected from the group consisting of octyltrichlorosilane and octadecyltrichlorosilane.
26. The hybrid monolith material of claim 3 or 4 having the formula
SiO₂/(R²_pR⁴_qSiO)_n or SiO₂/[R⁶(R²_rSiO)_m]_n wherein R² and R⁴ are independently C₁ - C₁₈ aliphatic, styryl, vinyl, propanol, or aromatic moieties, R⁶ is a substituted or

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- unsubstituted $C_1 - C_{18}$ alkylene, alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms, p and q are 0, 1 or 2, provided that $p+q = 1$ or 2, and that when $p+q=1$, $t=1.5$, and when $p+q=2$, $t=1$; r is 0 or 1, provided that when $r = 0$, $t = 1.5$, and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2, and n is a number from 0.03 to 1.
- 5 27. The hybrid monolith material of claim 26, wherein n is a number from 0.1 to 1
28. The hybrid monolith material of claim 26 having average pore diameters of about 100 to 300Å.
- 10 29. The hybrid monolith material of claim 26 wherein n is a number from 0.20 to 0.5.
30. The hybrid monolith material of claim 3 or 4 wherein said inorganic portion of said hybrid monolith material is selected from the group consisting of alumina, silica, titanium or zirconium oxides, and ceramic materials.
- 15 31. The hybrid monolith material of claim 3 or 4 wherein said inorganic portion of said hybrid monolith material is silica.
32. The hybrid material of claim 3 or 4, wherein said particles have been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.
- 20 33. The hybrid material of claim 3 or 4, wherein said particles have been surface modified by a combination of an organic group surface modifier and a polymeric coating surface modifier.
34. The hybrid material of claim 3 or 4, wherein said particles have been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface modifier.
- 25 35. The hybrid material of claim 3 or 4, wherein said particles have been surface modified via formation of an organic covalent bond between an organic group of the particle and a surface modifier.
36. The hybrid material of claim 3 or 4, wherein said particles have been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.
- 30 37. The hybrid material of claim 3 or 4, wherein said particles have been surface modified by a silanol group surface modifier.

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38. A method of preparation of a porous inorganic/organic hybrid monolith material, comprising porous inorganic/organic hybrid particles having a chromatographically-enhancing pore geometry, comprising the steps of

- a) forming porous inorganic/organic hybrid particles,
- 5 b) modifying the pore structure of said porous hybrid particles, and
- c) coalescing said porous hybrid particles to form a monolith material.

39. The method of claim 38, wherein the porous hybrid particles are coalesced by sintering.

40. The method of claim 38, wherein the porous hybrid particles are mixed with a
10 second material that is removed after coalescence of the porous hybrid particles.

41. The method of claim 40, wherein the second material is unbonded silica.

42. The method of claim 38, wherein said particles have been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and
15 combinations thereof.

43. The method of claim 38, wherein said particles have been surface modified by a polymeric coating surface modifier.

44. The method of claim 38, wherein said particles have been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.

20 45. The method of claim 38, wherein said particles have been surface modified by a combination of an organic group surface modifier and a polymeric coating surface modifier.

46. The method of claim 38, wherein said particles have been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface
25 modifier.

47. The method of claim 38, wherein said particles have been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.

48. The method of claim 38, wherein said particles have been surface modified by a
30 silanol group surface modifier.

49. The method of claim 38, wherein said particles have been surface modified via formation of an organic covalent bond between an organic group of the particle and a surface modifier.

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50. The method of claim 38 wherein said porous hybrid particles are prepared by prepolymerizing one or more organoalkoxysilanes and a tetraalkoxysilane to produce a polyorganoalkoxysiloxane, and preparing an aqueous suspension of said polyorganoalkoxysiloxane, and gelling in the presence of a base catalyst so as to produce
5 said porous hybrid particles.
51. The method of claim 38 wherein said porous hybrid particles are prepared by prepolymerizing one or more organotrialkoxysilanes and a tetraalkoxysilane to produce a polyalkyloxysiloxane, preparing an aqueous suspension of said polyalkyloxysiloxane, and gelling in the presence of a base catalyst so as to produce said porous hybrid
10 particles.
52. The method of claim 50 or 51 wherein said pore structure of said porous hybrid particles is modified by further including a surfactant or combination of different surfactants in said suspension, and by subjecting said porous hybrid particles to hydrothermal treatment.
- 15 53. The method of claim 50 or 51 wherein said pore structure of said porous hybrid particles is modified by further including a combination of different surfactants in said suspension, and by subjecting said porous hybrid particles to hydrothermal treatment.
54. The method of claim 52 wherein said surfactant or combination of surfactants are selected from the group consisting of Triton X-45, sodium dodecylsulfate,
20 tris(hydroxymethyl)aminomethane lauryl sulfate, and any combination thereof.
55. The method of claim 38 wherein said method further comprises surface modifying said porous hybrid particles.
56. The method of claim 50 wherein said prepolymerization step comprises hydrolyzing and condensing a mixture of one or more organoalkoxysilanes and a
25 tetraalkoxysilane in the presence of an acid catalyst to produce said polyalkyloxysiloxane.
57. The method of claim 51 wherein said prepolymerization step comprises hydrolyzing and condensing a mixture of one or more organotrialkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst to produce said
30 polyalkyloxysiloxane.
58. A method of preparation of a porous inorganic/organic hybrid monolith material, comprising porous inorganic/organic hybrid particles that have a chromatographically-enhancing pore geometry, comprising the steps of

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- a) forming porous inorganic/organic hybrid particles,
- b) modifying the pore structure of said porous hybrid particles,
- c) surface modifying said porous hybrid particles, and
- d) coalescing said porous hybrid particles to form a monolith material,

5 wherein said particles have been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.

59. The method of claim 58 wherein the surface modification step includes surface modifying said porous hybrid particles with a surface modifier having the formula
10 $Z_a(R')_b\text{Si-R}$, where $Z = \text{Cl, Br, I, C}_1 - \text{C}_5 \text{ alkoxy, dialkylamino or trifluoromethanesulfonate}$; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $\text{C}_1 - \text{C}_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.

60. The method of claim 58, wherein said particles have been surface modified by a
15 polymeric coating surface modifier.

61. The method of claim 58, wherein said particles have been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.

62. The method of claim 58, wherein said particles have been surface modified by a combination of an organic group surface modifier and a polymeric coating surface
20 modifier.

63. The method of claim 58, wherein said particles have been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface modifier.

64. The method of claim 58, wherein said particles have been surface modified by a
25 combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.

65. The method of claim 58, wherein said particles have been surface modified by a silanol group surface modifier.

66. The method of claim 58, wherein said particles have been surface modified via
30 formation of an organic covalent bond between an organic group of the particle and a surface modifier.

67. The method of claim 58, wherein the porous hybrid particles are coalesced by sintering.

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68. The method of claim 58, wherein the porous hybrid particles are mixed with a second material that is removed after coalescence of the porous hybrid particles.
69. The method of claim 68, wherein the second material is unbonded silica.
70. The method of claim 59 wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl, hexyl and cyclohexyl.
71. The method of claim 59 wherein said functionalizing group R is a C₁ – C₃₀ alkyl group.
72. The method of claim 59 wherein said functionalizing group R is a C₁ – C₂₀ alkyl group.
73. The method of claim 59 wherein said surface modifier is selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octyldimethylchlorosilane, and octadecyldimethylchlorosilane.
74. The method of claim 73 wherein said surface modifier is selected from the group consisting of octyltrichlorosilane and octadecyltrichlorosilane.
75. The method of claim 59, wherein said functionalizing group R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, or an alkyl or aryl group containing an embedded polar functionality.
76. The method of claim 55 wherein any free silanol groups remaining from said surface modification procedure are endcapped.
77. The method of claim 50 wherein the molar ratio of said organoalkoxysilane and tetraalkoxysilane is from about 0.5:1 to 0.2:1.
78. The method of claim 50 wherein the molar ratio of said organotrialkoxysilane and tetraalkoxysilane is from about 0.5:1 to 0.2:1.
79. The method of claim 38 wherein said porous hybrid particles have a specific surface area of about 50 to 800m²/g.
80. The method of claim 38 wherein said porous hybrid particles have a specific surface area of about 100 to 350m²/g.
81. The method of claim 38 wherein said porous hybrid particles have specific pore volumes of about 0.25 to 1.5 cm³/g.
82. The method of claim 38 wherein said porous hybrid particles have specific pore volumes of about 0.4 to 1.2 cm³/g.

83. The method of claim 38 wherein said porous hybrid particles have an average pore diameter of about 50 to 500 Å.
84. The method of claim 38 wherein said porous hybrid particles have a micropore surface area of less than about 110 m²/g.
- 5 85. The method of claim 38 wherein said porous hybrid particles have an average pore diameter of about 100 to 300 Å.
86. The method of claim 38, wherein said porous hybrid particles have a specific surface area of about 50 to 800 m²/g, said porous hybrid particles have specific pore volumes of about 0.25 to 1.5 cm³/g, and said porous hybrid particles have an average
10 pore diameter of about 50 to 500 Å.
87. The method of claim 50 wherein said suspension further comprises a porogen.
88. The method of claim 87 wherein said porogen is toluene.
89. The method of claim 50 wherein said tetraalkoxysilane has the formula Si(OR¹)₄, where R¹ is a C₁ - C₃ alkyl moiety.
- 15 90. The method of claim 50 wherein said tetraalkoxysilane is selected from the group consisting of tetramethoxysilane and tetraethoxysilane.
91. The method of claim 50 wherein said organoalkoxysilane has the formula R²Si(OR¹)₃ or R⁶[Si(OR¹)₃]_m where R² is a C₁ - C₁₈ aliphatic, styryl, vinyl, propanol or aromatic moiety, R¹ is a C₁ - C₄ alkyl moiety, R⁶ is a C₁ - C₁₈ alkylene, alkenylene,
20 alkynylene or arylene moiety bridging two or more silicon atoms, and m is an integer greater than or equal to two.
92. The method of claim 50 wherein said organotrialkoxysilane has the formula R²Si(OR¹)₃, where R² is a C₁ - C₁₈ aliphatic or aromatic moiety and R¹ is a C₁ - C₄ alkyl moiety.
- 25 93. The method of claim 50 wherein said base catalyst is free of alkali or alkaline earth metal cations.
94. The method of claim 93 wherein said base catalyst is ammonium hydroxide.
95. The method of claim 91 wherein R² is methyl, ethyl, phenyl, vinyl, methacryloxypropyl, or styrylethyl and R¹ is ethyl; or R⁶ is a bridging ethylene group, m
30 = 2, and R¹ is ethyl or methyl.
96. The method of claim 38 wherein said porous inorganic/organic hybrid particles have the formula SiO₂/(R²_pR⁴_qSiO_t)_n or SiO₂/[R⁶(R²_rSiO_t)_m]_n wherein R² and R⁴ are independently C₁ - C₁₈ aliphatic, styryl, vinyl, propanol, or aromatic moieties, R⁶ is a substituted or unsubstituted C₁ - C₁₈ alkylene, alkenylene, alkynylene or arylene moiety

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bridging two or more silicon atoms, p and q are 0, 1 or 2, provided that $p+q = 1$ or 2, and that when $p+q=1$, $t=1.5$, and when $p+q=2$, $t=1$; r is 0 or 1, provided that when $r = 0$, $t = 1.5$, and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2, and n is a number from 0.03 to 1.

- 5 97. The method of claim 96, wherein n is a number from 0.1 to 1
98. The method of claim 96 wherein said porous inorganic/organic hybrid particles have average pore diameters of about 100 to 300Å.
99. The method of claim 96 wherein n is a number from 0.2 to 0.5.
100. A separations device comprising a porous inorganic/organic hybrid monolith
- 10 material having a chromatographically-enhancing pore geometry.
101. The separations device of claim 100, wherein the monolith material further comprises coalesced porous inorganic/organic hybrid particles having a chromatographically-enhancing pore geometry.
102. The separations device of claim 100, wherein said porous hybrid monolith
- 15 material has a specific surface area of about 100 to 350m²/g.
103. The separations device of claim 100 wherein said porous hybrid monolith material has a micropore surface area of less than about 110 m²/g.
- 104 The separations device of claim 101, wherein said porous hybrid monolith material has a specific pore volumes of about 0.4 to 1.2 cm³/g.
- 20 105. The separations device of claim 101, wherein said porous hybrid monolith material has a micropore surface area of less than about 105 m²/g.
106. The separations device of claim 101, wherein said porous hybrid monolith material has a micropore surface area of less than about 80 m²/g.
107. The separations device of claim 101, said porous hybrid monolith material has a
- 25 micropore surface area of less than about 50 m²/g.
108. The separations device of claim 101, wherein said porous hybrid monolith material has average pore diameter of about 100 to 300Å.
109. The separations device of claim 100 or 101, wherein said device is selected from the group consisting of chromatographic columns, thin layer plates, filtration
- 30 membranes, sample cleanup devices, and microtiter plates.
110. The separations device of claim 101, wherein said porous hybrid particles have a specific surface area of about 100 to 350m²/g.

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111. The separations device of claim 101 wherein said porous hybrid particles have a micropore surface area of less than about $110 \text{ m}^2/\text{g}$.
112. The separations device of claim 101, wherein said porous hybrid particles have specific pore volumes of about 0.4 to $1.2 \text{ cm}^3/\text{g}$.
- 5 113. The separations device of claim 101, wherein said porous hybrid particles have a micropore surface area of less than about $105 \text{ m}^2/\text{g}$.
114. The separations device of claim 101, wherein said porous hybrid particles have a micropore surface area of less than about $80 \text{ m}^2/\text{g}$.
115. The separations device of claim 101, said porous hybrid particles have a
10 micropore surface area of less than about $50 \text{ m}^2/\text{g}$.
116. The separations device of claim 101, wherein said porous hybrid particles have an average pore diameter of about 100 to 300 \AA .
117. A separations device comprising a porous inorganic/organic hybrid monolith material, wherein said monolith material is comprised of coalesced porous
15 inorganic/organic hybrid particles, and wherein said particles have been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.
118. The separations device of claim 117, wherein the porous hybrid particles have a
20 chromatographically-enhancing pore geometry and have been surface modified with a surface modifier having the formula $\text{Z}_a(\text{R}')_b\text{Si-R}$, where $\text{Z} = \text{Cl, Br, I, C}_1 - \text{C}_5 \text{ alkoxy, dialkylamino or trifluoromethanesulfonate}$; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $\text{C}_1 - \text{C}_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.
- 25 119. The separations device of claim 118, wherein said surface modifier is selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octyldimethylchlorosilane, and octadecyldimethylchlorosilane.
120. The separations device of claim 119, wherein said surface modifier is selected from the group consisting of octyltrichlorosilane and octadecyltrichlorosilane.
- 30 121. The separations device of claim 118, wherein said functionalizing group R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, or an alkyl or aryl group containing an embedded polar functionality.

122. The separations device of claim 118, wherein said functionalizing group R is a $C_1 - C_{30}$ alkyl group.
123. The separations device of claim 118, wherein said functionalizing group R is a $C_1 - C_{20}$ alkyl group.
- 5 124. The separations device of claim 101, wherein said porous hybrid particles have the formula $SiO_2/(R^2_p R^4_q SiO_t)_n$ or $SiO_2/[R^6(R^2_r SiO_t)_m]_n$ wherein R^2 and R^4 are independently $C_1 - C_{18}$ aliphatic, styryl, vinyl, propanol, or aromatic moieties, R^6 is a substituted or unsubstituted $C_1 - C_{18}$ alkylene, alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms, p and q are 0, 1 or 2, provided that $p+q = 1$ or 2, and
 10 that when $p+q=1$, $t=1.5$, and when $p+q=2$, $t=1$; r is 0 or 1, provided that when $r = 0$, $t = 1.5$, and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2, and n is a number from 0.03 to 1.
125. The separations device of claim 124, wherein n is a number from 0.1 to 1.
126. The separations device of claim 124, wherein said porous hybrid particles have
 15 average pore diameters of about 100 to 300Å.
127. The separation device of claim 124 wherein n is a number from 0.2 to 0.5.
128. The separations device of claim 101 wherein said inorganic portion of said hybrid monolith material is selected from the group consisting of alumina, silica, titanium or zirconium oxides, and ceramic materials.
- 20 129. The separations device of claim 101 wherein said inorganic portion of said hybrid monolith material is silica.
130. A chromatographic column having improved lifetime, comprising
- a) a column having a cylindrical interior for accepting a monolith material of porous inorganic/organic hybrid material, and
- 25 b) a chromatographic bed comprising a porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry of the formula $SiO_2/(R^2_p R^4_q SiO_t)_n$ or $SiO_2/[R^6(R^2_r SiO_t)_m]_n$ wherein R^2 and R^4 are independently $C_1 - C_{18}$ aliphatic, styryl, vinyl, propanol, or aromatic moieties, R^6 is a substituted or unsubstituted $C_1 - C_{18}$ alkylene, alkenylene, alkynylene or arylene moiety bridging two
 30 or more silicon atoms, p and q are 0, 1 or 2, provided that $p+q = 1$ or 2, and that when $p+q=1$, $t=1.5$, and when $p+q=2$, $t=1$; r is 0 or 1, provided that when $r = 0$, $t = 1.5$, and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2, and n is a number from 0.03 to 1.

131. A chromatographic column having improved lifetime, comprising
- a) a column having a cylindrical interior for accepting a monolith material of porous inorganic/organic hybrid material, and
 - b) a chromatographic bed comprising a porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry, wherein said monolith material has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.
132. The chromatographic column of claim 131 that has been surface modified with a surface modifier having the formula $Z_a(R')_b\text{Si-R}$, where $Z = \text{Cl, Br, I, C}_1 - \text{C}_5 \text{ alkoxy, dialkylamino or trifluoromethanesulfonate}$; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $\text{C}_1 - \text{C}_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.
133. The chromatographic column of claim 130 or 131, wherein the porous inorganic/organic hybrid monolith material is prepared from coalesced porous hybrid particles, wherein the porous hybrid particles have a chromatography-enhancing pore geometry and average pore diameters of about 100 to 300 Å, and said porous hybrid particles of hybrid silica have been surface modified
134. The chromatographic column of claim 130, wherein n is a number from 0.1 to 1.
135. A method of preparation of a porous inorganic/organic hybrid monolith material, comprising coalesced porous particles of hybrid silica having a chromatography-enhancing pore geometry, comprising the steps of
- a) prepolymerizing a mixture of one or more organoalkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst to produce a polyorganoalkoxysiloxane;
 - b) preparing an aqueous suspension of said polyorganoalkoxysiloxane, said suspension further comprising a surfactant or combination of surfactants, and gelling in the presence of a base catalyst so as to produce porous hybrid particles;
 - c) modifying the pore structure of said porous hybrid particles by hydrothermal treatment; and
 - d) coalescing said porous hybrid particles to form a monolith material thereby preparing a porous inorganic/organic hybrid monolith material.

136. The method of claim 135 wherein the molar ratio of said organotrialkoxysilane and tetraalkoxysilane is from about 0.5:1 to 0.2:1.
137. The method of claim 135 wherein said porous hybrid particles have a specific surface area of about 75 to 600 m²/g.
- 5 138. The method of claim 135 wherein said porous hybrid particles have a specific surface area of about 100 to 350 m²/g.
139. The method of claim 135 wherein said porous hybrid particles have a micropore surface area of less than about 110 m²/g.
140. The method of claim 135 wherein said porous hybrid particles have specific pore
10 volumes of about 0.4 to 1.2 cm³/g.
141. The method of claim 135, wherein said porous hybrid particles have a micropore surface area of less than about 105 m²/g.
142. The method of claim 135, wherein said porous hybrid particles have a micropore surface area of less than about 80 m²/g.
- 15 143. The method of claim 135, wherein said porous hybrid particles have a micropore surface area of less than about 50 m²/g.
144. The method of claim 135 wherein said porous hybrid particles have an average pore diameter of about 50 to 500 Å.
145. The method of claim 135 wherein said porous hybrid particles have an average
20 pore diameter of about 100 to 300 Å.
146. The method of claim 135 wherein said surfactant is an alkylphenoxypolyethoxyethanol.
147. The method of claim 135 wherein said suspension further comprises a porogen.
148. The method of claim 135 wherein said tetraalkoxysilane is selected from the
25 group consisting of tetramethoxysilane and tetraethoxysilane.
149. The method of claim 135, wherein said porous hybrid particles have the formula SiO₂/(R²_pR⁴_qSiO_t)_n or SiO₂/[R⁶(R²_rSiO_t)_m]_n wherein R² and R⁴ are independently C₁ - C₁₈ aliphatic, styryl, vinyl, propanol, or aromatic moieties, R⁶ is a substituted or unsubstituted C₁ - C₁₈ alkylene, alkenylene, alkynylene or arylene moiety bridging two
30 or more silicon atoms, p and q are 0, 1 or 2, provided that p+q = 1 or 2, and that when p+q=1, t=1.5, and when p+q=2, t=1; r is 0 or 1, provided that when r = 0, t = 1.5, and when r = 1, t = 1; m is an integer greater than or equal to 2, and n is a number from 0.03 to 1.

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150. The method of claim 135, wherein n is a number from 0.1 to 1.
151. The method of claim 149, wherein said porous hybrid particles have average pore diameters of about 100 to 300Å.
152. The method of claim 149 wherein n is a number from 0.2 to 0.5.
- 5 153. A porous inorganic/organic hybrid monolith material comprising coalesced porous hybrid particles of hybrid silica having a chromatographically-enhancing pore geometry, produced by the process of
- 10 a) prepolymerizing a mixture of one or more organoalkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst to produce a polyorganoalkoxysiloxane;
 - b) preparing an aqueous suspension of said polyorganoalkoxysiloxane, said suspension further comprising a surfactant or a combination of surfactants, and gelling in the presence of a base catalyst so as to produce porous hybrid particles;
 - 15 c) modifying the pore structure of said porous hybrid particles by hydrothermal treatment; and
 - d) coalescing said porous hybrid particles to form a monolith material.
154. The hybrid monolith material of claim 153 wherein the molar ratio of said organoalkoxysilane and tetraalkoxysilane is from about 0.5:1 to 0.2:1.
- 20 155. The hybrid monolith material of claim 153 wherein said porous hybrid particles have a specific surface area of about 75 to 600m²/g.
156. The hybrid monolith material of claim 153 wherein said porous hybrid particles have a specific surface area of about 100 to 350m²/g.
157. The hybrid monolith material of claim 153 wherein said porous hybrid particles
- 25 have specific pore volumes of about 0.4 to 1.2 cm³/g.
158. The hybrid monolith material of claim 153 wherein said porous hybrid particles have a micropore surface area of less than about 110 m²/g.
159. The hybrid monolith material of claim 153, wherein said porous hybrid particles have a micropore surface area of less than about 105 m²/g.
- 30 160. The hybrid monolith material of claim 153, wherein said porous hybrid particles have a micropore surface area of less than about 80 m²/g.
161. The hybrid monolith material of claim 153, wherein said porous hybrid particles have a micropore surface area of less than about 50 m²/g.

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162. The hybrid monolith material of claim 153 wherein said porous hybrid particles have an average pore diameter of about 50 to 500Å.
163. The hybrid monolith material of claim 153 wherein said porous hybrid particles have an average pore diameter of about 100 to 300Å.
- 5 164. The hybrid monolith material of claim 153 wherein said surfactant is an alkylphenoxypolyethoxyethanol.
165. The hybrid monolith material of claim 153 wherein said suspension further comprises a porogen.
- 10 166. The hybrid monolith material of claim 153 wherein said tetraalkoxysilane is selected from the group consisting of tetramethoxysilane and tetraethoxysilane.
167. The hybrid monolith material of claim 153, having the formula $\text{SiO}_2/(\text{R}^2_p\text{R}^4_q\text{SiO})_n$ or $\text{SiO}_2/[\text{R}^6(\text{R}^2_r\text{SiO})_m]_n$ wherein R^2 and R^4 are independently C_1 - C_{18} aliphatic, styryl, vinyl, propanol, or aromatic moieties, R^6 is a substituted or unsubstituted C_1 - C_{18} alkylene, alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms, p and q are 0, 1 or 2, provided that $p+q = 1$ or 2, and that when $p+q=1$, $t=1.5$, and when $p+q=2$, $t=1$; r is 0 or 1, provided that when $r = 0$, $t = 1.5$, and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2, and n is a number from 0.03 to 1.
- 15 168. The hybrid monolith material of claim 167, wherein said porous hybrid particles have average pore diameters of about 100 to 300Å.
- 20 169. The hybrid monolith material of claim 167 wherein n is a number from 0.20 to 0.5.
170. The hybrid monolith material of claim 167, wherein n is a number from 0.1 to 1.
171. A porous inorganic/organic hybrid monolith material having a
- 25 chromatographically-enhancing pore geometry, wherein said material contains a plurality of macropores sufficient to result in reduced backpressure at chromatographically-useful flow rates.
172. The hybrid monolith material of claim 171, wherein the macropores are pores with a pore diameter larger than about 0.05 μm .
- 30 173. A porous inorganic/organic hybrid monolith material, having a chromatographically-enhancing pore geometry, wherein said monolith material has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.

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174. The hybrid monolith material of claim 173, wherein said monolith material has been surface modified with a surface modifier having the formula $Z_a(R')_bSi-R$, where $Z = Cl, Br, I, C_1 - C_5$ alkoxy, dialkylamino or trifluoromethanesulfonate; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $C_1 - C_6$ straight, cyclic or
 5 branched alkyl group, and R is a functionalizing group.

175. The hybrid monolith material of claim 172 or 174, wherein said monolith has been surface modified by a polymeric coating surface modifier.

176. The hybrid monolith material of claim 174 wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl,
 10 hexyl and cyclohexyl.

177. The hybrid monolith material of claim 174, wherein the functionalizing group R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, or an alkyl or aryl group containing an embedded polar functionality.

178. The hybrid monolith material of claim 177, wherein said functionalizing group R is a $C_1 - C_{30}$ alkyl group.

179. The hybrid monolith material of claim 177, wherein said functionalizing group R is a $C_1 - C_{20}$ alkyl group.

180. The hybrid monolith material of claim 174, wherein said surface modifier is
 20 selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octyldimethylchlorosilane, octadecyldimethylchlorosilane, and octadecyltrimethoxysilane.

181. The hybrid monolith material of claim 180, wherein said surface modifier is selected from the group consisting of octyltrichlorosilane and octadecyltrichlorosilane.

25 182. The hybrid monolith material of claim 180, wherein said surface modifier is octadecyltrichlorosilane.

183. The hybrid monolith material of claim 171 or 173 having the formula $SiO_2/(R^2_p R^4_q SiO_t)_n$ or $SiO_2/[R^6_r (R^2_r SiO_t)_m]_n$ wherein R^2 and R^4 are independently $C_1 - C_{18}$ aliphatic, styryl, vinyl, propanol, or aromatic moieties, R^6 is a substituted or
 30 unsubstituted $C_1 - C_{18}$ alkylene, alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms, p and q are 0, 1 or 2, provided that $p+q = 1$ or 2, and that when $p+q=1$, $t=1.5$, and when $p+q=2$, $t=1$; r is 0 or 1, provided that when $r = 0$, $t = 1.5$, and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2, and n is a number from 0.03 to 1.

35 184. The hybrid monolith material of claim 183, wherein n is a number from 0.1 to 1

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185. The hybrid monolith material of claim 183 wherein n is a number from 0.2 to 0.5.
186. The hybrid monolith material of claim 171 or 173 wherein said inorganic portion of said hybrid monolith material is selected from the group consisting of alumina, silica, titanium or zirconium oxides, and ceramic materials.
187. The hybrid monolith material of claim 171 or 173 wherein said inorganic portion of said hybrid monolith material is silica.
188. The hybrid monolith material of claim 171 or 174, wherein said monolith material has been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.
189. The hybrid monolith material of claim 171 or 174, wherein said monolith material has been surface modified by a combination of an organic group surface modifier and a polymeric coating surface modifier.
190. The hybrid monolith material of claim 171 or 174, wherein said monolith material has been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface modifier.
191. The hybrid monolith material of claim 171 or 174, wherein said monolith material has been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.
192. The hybrid monolith material of claim 171 or 174, wherein said monolith material has been surface modified by a silanol group surface modifier.
193. The hybrid monolith material of claim 171 or 174, wherein said monolith material has been surface modified via formation of an organic covalent bond between an organic group of the particle and a surface modifier.
194. A method of preparation of a porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry, comprising the steps of
- a) forming a porous inorganic/organic monolith material and
 - b) modifying the pore structure of said porous monolith material.
195. The method of claim 194, wherein said monolith material has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.
196. The method of claim 195, wherein said monolith has been surface modified by a polymeric coating surface modifier.

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197. The method of claim 195, wherein said monolith material has been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.
198. The method of claim 195, wherein said monolith material has been surface
5 modified by a combination of an organic group surface modifier and a polymeric coating surface modifier.
199. The method of claim 195, wherein said monolith material has been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface modifier.
- 10 200. The method of claim 195, wherein said monolith material has been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.
201. The method of claim 195, wherein said monolith material has been surface modified by a silanol group surface modifier.
- 15 202. The method of claim 195, wherein said monolith material has been surface modified via formation of an organic covalent bond between an organic group of the particle and a surface modifier.
203. The method of claim 194 wherein said monolith material is prepared by
- 20 a) preparing an aqueous solution of a mixture of one or more organoalkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst, and a surfactant or combination of surfactants to produce a polyorganoalkoxysiloxane;
- b) incubating said solution, resulting in a three-dimensional gel having a continuous, interconnected pore structure,
- 25 c) aging the gel at a controlled pH and temperature to yield a solid monolith material, and
- d) rinsing the monolith material with an aqueous basic solution at an elevated temperature.
204. The method of claim 194 wherein said monolith material are prepared by
- 30 a) preparing an aqueous solution of a mixture of one or more organotrialkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst, and a surfactant or combination of surfactants to produce a polyorganoalkoxysiloxane;

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- b) incubating said solution, resulting in a three-dimensional gel having a continuous, interconnected pore structure,
- c) aging the gel at a controlled pH and temperature to yield a solid monolith material, and
- 5 d) rinsing the monolith material with an aqueous basic solution at an elevated temperature.

205. The method of claim 203 or 204, wherein said surfactant or combination of surfactants are selected from the group consisting of Pluronic P-105, Pluronic P-123, Triton 405, and Triton X-100, and any combination thereof.

- 10 206. The method of claim 203 wherein said pore structure of said monolith material is modified by hydrothermal treatment further, rinsed with water followed by a solvent exchange, dried at room temperature, and dried at elevated temperature under vacuum.

207. The method of claim 194 wherein said method further comprises surface modifying said porous monolith materials.

- 15 208. A method of preparation of a porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry, comprising the steps of

- a) forming a porous inorganic/organic monolith material,
- b) modifying the pore structure of said porous monolith material, and
- c) modifying the surface of said porous monolith material,

- 20 wherein said monolith material has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.

209. The method of claim 208, wherein the surface modification step includes surface modifying said porous monolith material with a surface modifier having the formula
- 25 $Z_a(R')_b\text{Si-R}$, where $Z = \text{Cl, Br, I, C}_1 - \text{C}_5 \text{ alkoxy, dialkylamino or trifluoromethanesulfonate}$; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $\text{C}_1 - \text{C}_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.

210. The method of claim 209, wherein said monolith has been surface modified by a
- 30 polymeric coating surface modifier.

211. The method of claim 209, wherein said monolith material has been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.

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212. The method of claim 209, wherein said monolith material has been surface modified by a combination of an organic group surface modifier and a polymeric coating surface modifier.
213. The method of claim 209, wherein said monolith material has been surface
5 modified by a combination of a silanol group surface modifier and a polymeric coating surface modifier.
214. The method of claim 209, wherein said monolith material has been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.
- 10 215. The method of claim 209, wherein said monolith material has been surface modified by a silanol group surface modifier.
216. The method of claim 209, wherein said monolith material has been surface modified via formation of an organic covalent bond between an organic group of the particle and a surface modifier.
- 15 217. The method of claim 209 wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl, hexyl and cyclohexyl.
218. The method of claim 209 wherein said functionalizing group R is a C₁ – C₃₀ alkyl group.
- 20 219. The method of claim 209 wherein said functionalizing group R is a C₁ – C₂₀ alkyl group.
220. The method of claim 209 wherein said surface modifier is selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octyldimethylchlorosilane, octadecyldimethylchlorosilane, and
25 octadecyltrimethoxysilane.
221. The method of claim 220 wherein said surface modifier is selected from the group consisting of octyltrichlorosilane and octadecyltrichlorosilane.
222. The method of claim 220 wherein said surface modifier is octadecyltrichlorosilane.
- 30 223. The method of claim 209, wherein said functionalizing group R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, or an alkyl or aryl group containing an embedded polar functionality.

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224. The method of claim 207 wherein any free silanol groups remaining from said surface modification procedure are endcapped.
225. The method of claim 203 wherein the molar ratio of said organoalkoxysilane and tetraalkoxysilane is from about 0.5:1 to 0.2:1.
- 5 226. The method of claim 204 wherein the molar ratio of said organotrialkoxysilane and tetraalkoxysilane is from about 0.5:1 to 0.2:1.
227. The method of claim 203 or 204 wherein said tetraalkoxysilane has the formula $\text{Si}(\text{OR}^1)_4$, where R^1 is a $\text{C}_1 - \text{C}_3$ alkyl moiety.
228. The method of claim 203 or 204 wherein said tetraalkoxysilane is selected from
10 the group consisting of tetramethoxysilane and tetraethoxysilane.
229. The method of claim 203 wherein said organoalkoxysilane has the formula $\text{R}^2\text{Si}(\text{OR}^1)_3$ or $\text{R}^6[\text{Si}(\text{OR}^1)_3]_m$ where R^2 is a $\text{C}_1 - \text{C}_{18}$ aliphatic, styryl, vinyl, propanol, or aromatic moiety, R^1 is a $\text{C}_1 - \text{C}_4$ alkyl moiety, R^6 is a $\text{C}_1 - \text{C}_{18}$ alkylene, alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms, and m is an integer
15 greater than or equal to two.
230. The method of claim 204 wherein said organotrialkoxysilane has the formula $\text{R}^2\text{Si}(\text{OR}^1)_3$, where R^2 is a $\text{C}_1 - \text{C}_{18}$ aliphatic or aromatic moiety and R^1 is a $\text{C}_1 - \text{C}_4$ alkyl moiety.
231. The method of claim 203 or 204 wherein said aqueous basic solution is
20 ammonium hydroxide.
232. The method of claim 229 wherein R^2 is methyl, ethyl, phenyl, vinyl, methacryloxypropyl, or styrylethyl and R^1 is ethyl; or R^6 is a bridging ethylene group, $m = 2$, and R^1 is ethyl.
233. The method of claim 194 wherein said porous inorganic/organic hybrid monolith
25 material has the formula $\text{SiO}_2/(\text{R}^2\text{R}^4\text{SiO}_t)_n$ or $\text{SiO}_2/[\text{R}^6(\text{R}^2\text{SiO}_t)_m]_n$ wherein R^2 and R^4 are independently $\text{C}_1 - \text{C}_{18}$ aliphatic, styryl, vinyl, propanol, or aromatic moieties, R^6 is a substituted or unsubstituted $\text{C}_1 - \text{C}_{18}$ alkylene, alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms, p and q are 0, 1 or 2, provided that $p+q = 1$ or 2, and that when $p+q=1$, $t=1.5$, and when $p+q=2$, $t=1$; r is 0 or 1, provided that when $r = 0$, $t =$
30 1.5 , and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2, and n is a number from 0.03 to 1.
234. The method of claim 233, wherein n is a number from 0.1 to 1
235. The method of claim 233 wherein n is a number from 0.20 to 0.5.

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236. A separations device comprising a porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry, wherein said monolith material has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.

237. The method of claim 236, wherein said monolith material has been surface modified with a surface modifier having the formula $Z_a(R')_b\text{Si-R}$, where $Z = \text{Cl, Br, I, C}_1 - \text{C}_5 \text{ alkoxy, dialkylamino or trifluoromethanesulfonate}$; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $\text{C}_1 - \text{C}_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.

238. A method of preparation of a porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry comprising

- a) preparing an aqueous solution of a mixture of one or more organoalkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst, and a surfactant or combination of surfactants to produce a polyorganoalkoxysiloxane;
- b) incubating said solution, resulting in a three-dimensional gel having a continuous, interconnected pore structure,
- c) aging the gel at a controlled pH and temperature to yield a solid monolith material,
- d) rinsing the monolith material with an aqueous basic solution at an elevated temperature,
- e) modifying the pore structure of said monolith material by hydrothermal treatment,
- f) rinsing the monolith material with water followed by a solvent exchange, and
- g) drying the monolith material at room temperature drying and at an elevated temperature under vacuum.

thereby preparing a porous inorganic/organic hybrid monolith material.

239. The method of claim 238, wherein the solvent is exchanged to methanol

240. A porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry, produced by the process of

- 5 a) preparing an aqueous solution of a mixture of one or more organotrialkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst, and a surfactant or combination of surfactants to produce a polyorganoalkoxysiloxane;
- b) incubating said solution, resulting in a three-dimensional gel having a continuous, interconnected pore structure,
- c) aging the gel at a controlled pH and temperature to yield a solid monolith material, and
- 10 d) rinsing the monolith material with an aqueous basic solution at an elevated temperature
- e) modifying the pore structure of said monolith material by hydrothermal treatment,
- f) rinsing the monolith material with water followed by a solvent exchange, and
- g) drying the monolith material at room temperature drying and at an elevated temperature under vacuum.
- 15 241. The hybrid monolith material of claim 240, wherein the solvent is exchanged to methanol, ethanol, acetonitrile, tetrahydrofuran, or hexane and the elevated temperature is about 70 to 120°C.
242. The hybrid monolith material of claim 241, wherein the solvent is exchanged to methanol and the elevated temperature is about 100°C.
- 20 243. The hybrid monolith material of claim 238, wherein the organoalkoxysilane is methyltrimethoxysilane and the tetraalkoxysilane is tetramethoxysilane.
244. The hybrid monolith material of claim 238, wherein the organoalkoxysilane is 1,2-bis-(trimethoxysilyl)ethane and the tetraalkoxysilane is tetramethoxysilane.
- 25 245. The hybrid monolith material of claim 238, wherein the organoalkoxysilane is methacryloxypropyltrimethoxysilane and the tetraalkoxysilane is tetramethoxysilane.
246. The hybrid monolith material of claim 238, wherein the acid catalyst is a solution of acetic acid.
247. The hybrid monolith material of claim 238, wherein the acid catalyst is an aqueous solution of acetic acid.
- 30 248. The hybrid monolith material of claim 238, wherein the acetic acid is about 0.1 mM to 500 mM.

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249. The hybrid monolith material of claim 246, wherein the acetic acid is about 10 mM to 150 mM.
250. The hybrid monolith material of claim 246, wherein the acetic acid is about 50 mM to 120 mM.
- 5 251. The hybrid monolith material of claim 238, wherein the surfactant is Pluronic P-105.
252. The hybrid monolith material of claim 238, wherein the surfactant is Pluronic P-123.
253. The hybrid monolith material of claim 238, wherein the surfactant is Triton X-100.
- 10 254. The hybrid monolith material of claim 238, wherein the surfactant is Triton 405.
255. The hybrid monolith material of claim 238, wherein the surfactant concentration is about 3% and 15% by weight.
256. The hybrid monolith material of claim 238, wherein the surfactant concentration is about 7% to 12 % by weight.
- 15 257. The hybrid monolith material of claim 238, wherein the surfactant concentration is about 8% to 10% by weight.
258. The hybrid monolith material of claim 238, wherein the total concentration of organoalkoxysilane and tetraalkoxysilane is about <5g/ml.
- 20 259. The hybrid monolith material of claim 238, wherein the total concentration of organoalkoxysilane and tetraalkoxysilane is about <2g/ml.
260. The hybrid monolith material of claim 238, wherein the total concentration of organoalkoxysilane and tetraalkoxysilane is about < 1g/ml.
261. The hybrid monolith material of claim 238, wherein the incubation temperature is about 90°C to the point at which the solution physically freezes.
- 25 262. The hybrid monolith material of claim 238, wherein the incubation temperature is about 20°C to 70°C.
263. The hybrid monolith material of claim 238, wherein the incubation temperature is about 35°C to 60 °C.
- 30 264. The hybrid monolith material of claim 238, wherein gel is aged from about 5 hours to 10 days.
265. The hybrid monolith material of claim 238, wherein gel is aged from about 10 hours to 7 days.

266. The hybrid monolith material of claim 238, wherein gel is aged from about 2 days to 5 days.
267. The hybrid monolith material of claim 238, wherein gel is aged at pH of about 2-3.
- 5 268. The hybrid monolith material of claim 238, wherein gel is aged at about 20°C to 70°C.
269. The hybrid monolith material of claim 238, wherein gel is aged at about 35°C to 60 °C.
- 10 270. The hybrid monolith material of claim 238, wherein the aqueous basic solution is ammonium hydroxide.
271. The hybrid monolith material of claim 238, wherein the concentration of aqueous basic solution is from about 10^{-5} N to 1 N.
272. The hybrid monolith material of claim 238, wherein the concentration of aqueous basic solution is from about 10^{-4} N to 0.5 N.
- 15 273. The hybrid monolith material of claim 238, wherein the concentration of aqueous basic solution is from about 10^{-3} N to 0.1 N.
274. The hybrid monolith material of claim 238, wherein the elevated temperature of rinsing is from about 0°C to 80 °C.
- 20 275. The hybrid monolith material of claim 238, wherein the elevated temperature of rinsing is from about 20 °C to 70 °C.
276. The hybrid monolith material of claim 238, wherein the elevated temperature of rinsing is from about 40 °C to 60 °C.
277. The hybrid monolith material of claim 238, wherein the rinsing time is from about 1 to 6 days.
- 25 278. The hybrid monolith material of claim 238, wherein the rinsing time is from about 1.5 to 4.5 days.
279. The hybrid monolith material of claim 238, wherein the rinsing time is from about 2 to 3 days.
- 30 280. The hybrid monolith material of claim 238, wherein the hydrothermal treatment is at pH is from about 7.0 to 12.0.
281. The hybrid monolith material of claim 238, wherein the hydrothermal treatment is at pH from about 7.3 to 11.0.

282. The hybrid monolith material of claim 238, wherein the hydrothermal treatment is at pH from about 7.5 to 10.6.
283. The hybrid monolith material of claim 238, wherein the hydrothermal treatment is at 110 °C to 180 °C.
- 5 284. The hybrid monolith material of claim 238, wherein the hydrothermal treatment is at 120°C to 160°C.
285. The hybrid monolith material of claim 238, wherein the hydrothermal treatment is at 130 °C to 155 °C.
- 10 286. A porous inorganic/organic hybrid monolith material, comprising coalesced porous inorganic/organic hybrid particles having a chromatographically-enhancing pore geometry and a formula $\text{SiO}_2/[\text{C}_2\text{H}_4(\text{SiO}_{1.5})_2]_{0.25}$ wherein said hybrid particles have been surface modified with octadecyltrichlorosilane and wherein any free silanol groups remaining from said surface modification are endcapped with chlorotrimethylsilane.
- 15 287. A porous inorganic/organic hybrid monolith material comprising coalesced porous hybrid particles of hybrid silica having a chromatographically-enhancing pore geometry and a formula $\text{SiO}_2/[\text{C}_2\text{H}_4(\text{SiO}_{1.5})_2]_{0.25}$ produced by the process of
- a) prepolymerizing a 0.25/1.0 mole ratio mixture of bis(triethoxysilyl)ethane and tetraethoxysilane in the presence of 0.1 molar hydrochloric acid to produce a polyorganosiloxane;
 - 20 b) preparing an aqueous suspension of said polyorganoalkoxysiloxane, said suspension further comprising the surfactant Triton X-100, and gelling said suspension in the presence of an ammonium hydroxide so as to produce porous hybrid particles;
 - c) modifying the pore structure of said porous hybrid particles by
25 hydrothermal treatment at 155 °C for 20 h in 0.3 M tris(hydroxymethyl)aminomethane, pH adjusted to 9.80;
 - d) sizing to a nominal 2 μm particle diameter;
 - e) acid washing in a 1 molar hydrochloric acid solution;
 - f) further surface modifying with octadecyltrichlorosilane wherein any free
30 silanol groups remaining from said surface modification are endcapped with chlorotrimethylsilane; and
 - g) coalescing said porous hybrid particles to form a monolith material.

288. A porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry and a formula $\text{SiO}_2/[\text{CH}_3\text{SiO}_{1.5}]_{0.5}$ wherein said hybrid material has been surface modified with octadecyltrichlorosilane and wherein any free silanol groups remaining from said surface modification procedure
5 are endcapped with chlorotrimethylsilane and wherein said material contains a plurality of macropores sufficient to result in reduced backpressure at chromatographically-useful flow rates.

289. A porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry and a formula $\text{SiO}_2/[\text{CH}_3\text{SiO}_{1.5}]_{0.5}$,
10 produced by the process of

- a) preparing an aqueous solution of methyltrimethoxysilane and a tetramethoxysilane in the presence of a 0.07 molar acetic acid solution and the surfactant Pluronic P-105 or Triton X-100 to produce a polyorganoalkoxysiloxane;
- 15 a) incubating said solution for 3 days at 45 °C, resulting in a three-dimensional gel having a continuous, interconnected pore structure;
- b) aging the gel in 1 molar ammonium hydroxide at 60 °C for 3 days to yield a solid monolith material;
- c) rinsing the monolith material with water;
- 20 d) modifying the pore structure of said monolith material by hydrothermal treatment at 155 °C for 20 h in 0.1 molar tris(hydroxymethyl)aminomethane, pH adjusted to 8.0;
- e) rinsing the monolith material with water followed by a solvent exchange;
- f) acid washing the monolith material in 1 molar hydrochloric acid for 24 hours
25 at 98 °C;
- g) rinsing the monolith material with water followed by a solvent exchange;
- h) drying the monolith material at room temperature drying and at 80 °C under vacuum; and
- 30 i) further surface modifying with octadecyltrichlorosilane wherein any free silanol groups remaining from said surface modification are endcapped with chlorotrimethylsilane.

290. A porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry and a formula $\text{SiO}_2/[\text{C}_2\text{H}_4(\text{SiO}_{1.5})_2]_{0.25}$ wherein said hybrid material has been surface modified with octadecyltrichlorosilane

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and wherein any free silanol groups remaining from said surface modification procedure are endcapped with chlorotrimethylsilane and wherein said material contains a plurality of macropores sufficient to result in reduced backpressure at chromatographically-useful flow rates.

- 5 291. A porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry and a formula $\text{SiO}_2/[\text{C}_2\text{H}_4(\text{SiO}_{1.5})_2]_{0.25}$, produced by the process of
- 10 a) preparing an aqueous solution 1,2-bis(trimethoxysilyl)ethane and tetramethoxysilane in the presence of a 0.09 molar acetic acid solution and the surfactant Pluronic P-123 to produce a polyorganoalkoxysiloxane;
- b) incubating said solution for 2 days at 45 °C, resulting in a three-dimensional gel having a continuous, interconnected pore structure;
- c) aging the gel in 1 molar ammonium hydroxide at 60 °C for 2 days to yield a solid monolith material;
- 15 d) rinsing the monolith material with water;
- e) modifying the pore structure of said monolith material by hydrothermal treatment at 155 °C for 24 h in 0.1 M tris(hydroxymethyl)aminomethane, pH adjusted to 10.6;
- f) rinsing the monolith material with water followed by a solvent exchange;
- 20 g) acid washing the monolith material in 1 molar hydrochloric acid for 24 hours at 98 °C;
- h) rinsing the monolith material with water followed by a solvent exchange;
- i) drying the monolith material at room temperature drying and at 80 °C under vacuum, and
- 25 j) further surface modifying with octadecyltrichlorosilane wherein any free silanol groups remaining from said surface modification are endcapped with chlorotrimethylsilane.
292. A porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry and a formula $\text{SiO}_2/[\text{HOC}_3\text{H}_6\text{SiO}_{1.5}]_{0.15}$ wherein said hybrid material has been surface modified with dodecylisocyanate and wherein said material contains a plurality of macropores sufficient to result in reduced backpressure at chromatographically-useful flow rates.
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293. A porous inorganic/organic hybrid monolith material having a chromatographically-enhancing pore geometry and a formula $\text{SiO}_2/[\text{HOC}_3\text{H}_6\text{SiO}_{1.5}]_{0.15}$, produced by the process of

- 5 a) preparing an aqueous solution methacryloxypropyltrimethoxysilane and tetramethoxysilane in the presence of a 0.015 molar acetic acid solution and the surfactant Triton X-100 or Triton 405 to produce a polyorganoalkoxysiloxane;
- b) incubating said solution for 3 days at 45 °C, resulting in a three-dimensional gel having a continuous, interconnected pore structure;
- 10 c) aging the gel in 1 molar ammonium hydroxide at 60 °C for 3 days to yield a solid monolith material;
- d) rinsing the monolith material with water;
- e) modifying the pore structure of said monolith material by hydrothermal treatment at 155 °C for 24 h in 0.1 M tris(hydroxymethyl)aminomethane, pH
15 adjusted to 10.6;
- f) rinsing the monolith material with water followed by a solvent exchange;
- g) acid washing the monolith material in 1 molar hydrochloric acid for 24 hours at 98 °C;
- h) rinsing the monolith material with water followed by a solvent exchange;
- 20 i) drying the monolith material at room temperature drying and at 80 °C under vacuum, and
- j) further surface modifying with dodecylisocyanate.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/25193

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : D04H 1/00 13/00 3/00 5/00

US CL : 428/292.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/292.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,869,152 A (COLON) 09 February 1999 (09.02.1996), abstract, column 2, lines 36-68; column 3, lines 1-36; column 4, lines 25-65; column 6, lines 10-59 and column 10, lines 32-58.	1-4; 6-24; 28-7; 155-166; 168-172; 186 and 240-293
Y	US 6,090,477 A (BURCHELL et al) 18 July 2000 (18.07.2000) abstract and column 2, lines 53-68	1 and 3
Y	US 4,017,528 A (UNGER et al) 12 April 1977 (12.04.1977) abstract and column 2, line 7-column 4, line 68 and column 6, lines 21-68	1,3, 259-260, 287-293
Y	US 6,207,098 B1 (NAKANISHI et al) 27 March 2001 (27.03.2001) entire document	1-37, 153-193,240-293

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 November 2002 (01.11.2002)

Date of mailing of the international search report

27 NOV 2002

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/25193

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

PCT/US02/25193

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions that are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-37; 153-193 and 240-293, drawn to a porous inorganic/organic hybrid monolith.

Group II, claim(s) 38-99; 135-152 and 194-239, drawn to a method of preparation of a porous inorganic/organic hybrid monolith.

Group III, claim(s) 100-129, drawn to a separations device.

Group IV, claim(s) 130-134, drawn to a chromatographic column.

The inventions listed as Groups I-IV do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: Claim 1 is anticipated by U.S. Patent Number 5,869,152. Accordingly, the special technical feature linking the four inventions, a porous inorganic/organic hybrid monolith, does not provide a contribution over the prior art, and no single inventive concept exists. Therefore, restriction is appropriate.